行政院國家科學委員會專題研究計畫　成果報告

海水中有機膠體物質與微量元素互動反應研究(I)：有機硫醇物之分佈與重要性(2/2)

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計畫主持人：溫良碩

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行政院國家科學委員會補助專題研究計畫報告

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※※※※　海水中有機膠體物質與微量元素互動反應研究（一）※

※　　　　　：有機硫醇物之分佈與重要性

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計畫類別：□個別型計畫　　□整合型計畫

計畫編號：90－2611－M－002－004

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計畫主持人：溫良碩

共同主持人：

計畫參與人員：莊佳穎

本成果報告包括以下應繳交之附件：

□赴國外出差或研習心得報告一份

□赴大陸地區出差或研習心得報告一份

□出席國際學術會議心得報告及發表之論文各一份

□國際合作研究計畫國外研究報告書一份

執行單位：海科中心

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計畫中文摘要：

關鍵詞:：膠體、有機硫醇物、微量元素、元素種類

國際先進研究顯示，膠體對發生在海洋中的反應與機制過程影響重大；舉凡緩衝全球氣候變遷，生物地球化學交換與循環，微量元素清除與滯留，改變懸浮顆粒特性與沉積行爲，細菌對碳的利用與微生物環境變化等。爲能詳盡瞭解膠體對海洋的影響，當今國際海洋研究首要課題便是海洋膠體的分佈、組成、定性定量、反應與機制。

微量元素，特別是一些重金屬元素，不僅是海洋生物不可或缺的營養元素，當其濃度升高時，亦成爲它們的致命因子。微量元素當然更與污染物質息息相關，是研究環境污染無法忽略的重要繯結。現今科學界初步已知微量元素在海洋中的行爲，除了與其濃度與水體本身的物理化學性質有關外，更與其在於水體環境中的媒介、載體、種類密不可分。

過去研究學者皆著重於微量元素無機種類之研究，但是近來眾多證據顯示，溶解性有機物（包括膠體）對微量元素在海洋中的行爲有主要的影響，其中又以大分子的有機硫醇物(Thiols)與酸性多糖類(Acidic Polysaccharides)最爲重要。

本研究計劃的主要目的在於運用不同的分離技術與分析方法，並配合實驗設計進行整合研究，期望先以一年時間初步探討海水中膠體與有機硫醇物在一些海洋環境的分佈與種類，並了解其對不同類型微量元素（鋁、銀、銅、鐵、鎘、鎳）的基本互動機制，以便能夠對海水膠體主要組成與官能團的結構，和其對微量元素的機制過程提供完整詳盡資料。進而瞭解其作用如何影響海洋環境，爲目前國內與國際海洋學界提供嶄新研究資料，以達成全面性海洋科學研究與國際先進研究並駕齊驅、相互競逐的宗旨。

計畫英文摘要：

Keywords： Colloids, Thiols, Trace Elements, Speciation, Distribution

Recent studies indicated that colloidal organic matter has considerable potential for impacting upon many oceanic processes, such as oceanic buffering of global climate change, in biogeochemical conversions and cycling, in trace element scavenging, in latering the sedimentation behaviour of suspended particles, in carbon utilization by bacteria and in ther generation of microbial habitat. Central to understanding the roles of colloidal orgainc mater in oceanic processes are the needs to (1) quantify this fraction accurately (2) characterize the components, and (3) relate well-defined major components to relevant activity.

There is increasing evidence for the importance of organic matter complexation of trace elements in natural waters. One of the most important questions in marine and environmental chemistry is the identification of specific functional groups which are responsible for complexing a particular trace metal. The objectives include the determination of; (1) the concentrations and distributions of colloids in different marine waters; (2) the concentrations and distributions of dissolved, colloidal and particulate thiols in different marine waters; (3) complexation of metal ions to specific thiols in natural organic matter; (4) determination of the structure and stability of these biopolymers towards biological, chemical and photochemical degradation.

The approach consists of using instrumental methods (e.g., Cross-flow ultrafiltration, ion exchage, HPLC, GF-AAS, ICPMS). The proposed research is relevant to oceanography because thiols have a special role in aquatic organisms as metal sequestering and detoxification agents, thus regulating trace metal concentrations as well as their bioavailability and toxicity. These organic fibrils also

have a similar function in the extracellular mileu by forming flocs and biofilms, binding extracellular enzymes in their active forms, scavenging trace metals from the water, immobilizing toxic substances, altering the surface characteristics of suspended particles, and modifying the solubility of associated molecules.

計畫研究結果：

本計畫微量元素研究部份結果於去年本國海洋大會發表，『南海微量元素（Cd, Cu, Fe, Ni）之分佈與物種』，並於近日在法國尼斯舉辦之歐美聯合地球科學年會（EGS-AGU-EUG Joint Assembly, April 6~11, 2003, Nice）上發表詳細結果，期間獲世界頂級之微量元素研究人員（如：E. Boyle, R. Sherrel, J. Moffet, S. Emmerson, S. van den Berg, H. de Barr等人）之肯定，此份研究成果將於近日完稿並送審（Science；麻省理工學院 Edward Boyle 教授建議）。

研究結果摘要如下；

BIO-ACTIVE TRACE ELEMENTS (Cd, Cu, Fe, Ni) IN THE OLIGOTROPHIC SOUTH CHINA SEA

Bio-active trace elements (Cu, Ni, Cd, Fe) in seawater play a critical role in regulating oceanic phytoplankton growth and, hence, may influence global carbon cycle. However, their *in-situ* speciation and bio-reactivity are poorly understood. Dissolved copper and nickel are believed to be present in seawater predominantly as low molecular weight soluble organic complexes which are readily available to marine organism and immune from particle scavenging. Dissolved iron is believed to exist predominantly as high molecular weight colloidal species. Using ultraclean ultrafiltration and ion exchange/affinity chelating chemistry, we demonstrate that in the oligotrophic ocean waters, these four bio-active elements have distinctive characteristics of speciation and reactivity, even though they display similar nutrient-type distributions. For dissolved Cu, the concentration increased from 0.9 nM in the surface water to 3 nM at depths below 500m; for dissolved Ni, 2~9 nM; for dissolved Cd, 0.01~0.9 nM; for dissolved Fe, 0.1~0.6 nM. All four elements showed

a subsurface minimum around 60 m deep, which corresponded to the subsurface Chl *a* maximum, indicating strong biological interactions with these elements. Detailed analysis revealed distinct size distribution and chemical reactivity for each element. For Cu, more than 50% in surface water was in smaller than 1kDa labile forms; the strongly complexed inert form increased from 28% at surface to 50% below 500 meter; the colloidal form Cu decreased from 12% at surface to a minimum of 6% at 60 meter, and then gradually increased to 16% in deeper water. For Ni, more than 80% was in smaller than 1kDa labile form, and very small fraction (~5%) in colloidal from. For Cd, almost all dissolved fraction was in smaller than 1kDa labile form. As for Fe, its dynamic nature in water column caused by complicated bio-interactions was evident. This study indicated that, with preferential uptake of trace elements by different phytoplankton species, they in turn assisted in regulating the concentration of trace elements. The feedback mechanisms include exudation of high-affinity, relatively specific complexing ligands, which control the speciation of trace elements in the ocean. At least four major groups of ligand compounds are responsible for such regulations. Dissolved trace elements in seawater may be much more dynamic than previously thought and bio-interaction through colloidal aggregation and organic complexation must be considered in future studies of ocean elemental cycles.